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Thermal management techniques for enhancing hydrogen adsorption and desorption in metal hydride reactors: a short recent review

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Abstract. This manuscript presents a short recent review of various techniques used for thermal management enhancement in metal hydride reactors, emphasizing their effect on hydrogen adsorption and desorption. Mainly, the article highlights 4 techniques: The incorporation of various fin types, the integration of heat exchangers within the metal hydride reactor, the addition of heat transfer enhancing material into the MH bed, and the addition of phase change material (PCM). The analysis presented provides brief insightful information about the state of Metal hydride reactors now, laying the groundwork for future studies and advancements in this area.

1. Introduction

Energy is the main essential pillar required by various applications to function on a daily basis, and it is the current focus of millions of researchers [1]–[11]. With the massive increase in energy consumption, worries arose concerning severe environmental and health influences caused by the emissions of large amounts of greenhouse gases such as carbon dioxide, carbon monoxide, and NO_x [12]. As a result, research is oriented towards renewable energy sources [13]. One of the most evolving alternatives is the use of hydrogen as an energy source and storage medium [14] due to its high energy density reaching 140 MJ/kg [15]. Plenty of research were conducted in the domain of hydrogen energy. Roy and Pramanik [16] provided an overview of hydrogen production methods, encompassing (1) the extraction from natural gases like hydrocarbons (e.g., Methane) through processes like partial oxidation and steam-methane reforming, (2) coal and biomass gasification, and (3) water electrolysis. Halder et al. [13] further classified hydrogen production technologies into electrochemical, thermochemical, and biochemical categories. In a separate review, Bosu and Rajamohan [17] explored recent advancements in hydrogen storage, outlining physical storage methods such as compression (gaseous state), cryogenic-

compression (liquid state), liquefaction (liquid state), and adsorption on activated carbon (solid state).

Nomenclature			
PCM	Phase change material	FT	Fins thickness
MH	Metal hydride	FN	Fins number
MHHST	Metal hydride hydrogen storage tank	TES	Thermal energy storage
EG	Expanded graphite	TCM	Thermochemical material
HT	Heat transfer	SC	Spiral cycle
HTF	Heat transfer fluid		

Additionally, hydrogen can be chemically stored in its solid state as metal hydride (MH). Notably, there is a growing interest in semiconductors like Silicon and Magnesium-based nanoparticles as room-temperature storage mediums [15]. Hydrogen applications are expanding into various everyday utilities, with a focus on areas such as hydrogen-based combined heat and power (CHP) industrial applications [18], fuel cells [13], chemical production of green hydrogen-based E-fuels [19], and contributions to the manufacturing, refining, and agricultural sectors [20]. These applications underscore hydrogen's potential as a promising energy source and carrier.

The present study concentrates on the field of hydrogen storage, providing a concise review of recent developments in metal hydride-hydrogen storage. Specifically, it examines the improvement of hydrogen adsorption and desorption through various techniques.

2. Thermal management techniques for MH

The performance of the metal hydride reactor is highly dependent on the thermal management of the reactor as the hydrogenation and dehydrogenation reactions are both bounded to heat transfer. For that, special treatment must be followed while designing the metal hydride hydrogen storage tank (MHHST), in regards to thermal management technique utilized, especially that the main problem encountering the metal hydride powder is the low thermal conductivity it has (~1 W/m.K.) [14]. There are mainly four main techniques used, as from the literature, to accompany the MHHST: (1) activating the MHHST by embedding an advanced heat exchanger encountering a heat transfer fluid (HTF); (2) addition of external/internal fins to the circumference of the tank; (3) addition of heat transfer (HT) enhancement material such as metal foams and expanded graphite (EG); and (4) coupling the MH bed with phase change materials (PCM). A hierarchy diagram showing major thermal management enhancement techniques available in the literature is depicted in **Figure 1**.

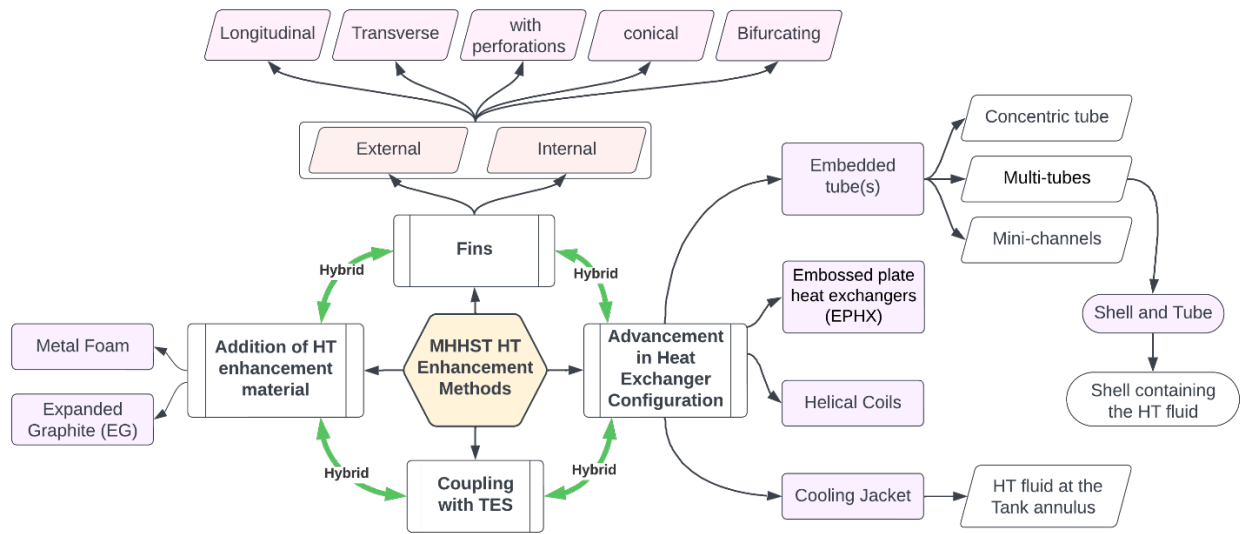


Figure 1 MHHST thermal management enhancement methods.

2.1 Advancement in heat exchangers configurations

Active techniques proved their resilience and effectiveness over passive techniques in regards to heat transfer, as forced convection is more efficient than natural convection. Research on managing the thermal performance of MH reactors involved a lot of studies on the utilization of heat exchangers with a suitable heat transfer fluid (HTF). Advancements in heat exchanger configurations and HTF incorporation emerged as the topic of hydrogen energy evolved. Mou et al. [21] investigated the performance of a MH reactor equipped with a coiled heat exchanger as shown in **Figure 2**. Numerical investigations showed that the reduction in HTF inlet temperature and thermal resistance between MH bed and coiled heat exchanger, and the increase in HTF flow rate and inlet operating pressure, all enhances hydrogen adsorption. Another study on helical coils heat exchanger was performed by Aadhithyan et al. [22]. The study aimed to obtain multi-optimized MH reactor. It was shown that the addition of fins to the coiled heat exchanger results in a reduction in the hydrogenation time that reaches 18% with an increase of 16% in thermal power, accompanied by a loss of 5.66% in weight ratio. Kumar et al. [23] investigated the effect of integrating multi-tube heat exchanger in a MH reactor for thermal management enhancement. The designed reactor was tested under different operating conditions. Urunkar and Patil [24] compared the performance of MH reactor utilizing different nanofluids as HTF for thermal management. The reactor design ensures the passing of HTF at the circumference of the MH bed forming a cooling jacket. Results showed that CuO/H₂O nanofluid was able to reduce the hydrogenation duration by 9.5% and enhance the rate of heat transfer by 10%.

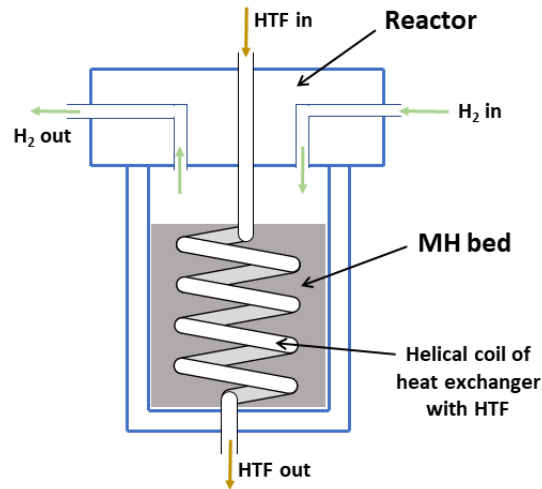


Figure 2 MH reactor with helical coil heat exchanger [21].

2.2 Equipping MH reactor with fins

A lot of studies were focused on the investigation of the effect of adding fins to the outer/inner shell of the MHHST for enhancing the thermal performance and thus the adsorption and desorption of hydrogen. The proposed designs of fins include: longitudinal/transverse, external/internal, helical, tree-shaped, hexagonal honeycomb, spiral...etc. Nyamsi et al. [25] designed a prototype and investigated its performance for a MH reactor integrated with basin-like heat exchanger for use with a fuel cell functioning as a power generator. The experimental study was followed with a numerical simulation [26] to test the performance of the reactor while varying different parameters. The designed heat exchanger contained internal transverse copper fins and external transverse aluminum fins for enhancing HT so that desorption of H₂ occurs at constant rate leading to a constant power output by the paired fuel cell. Results showed that dehydrogenation with graduate heating by hot air allows a stable Hydrogen flow rate to the paired FC without the need for a flow regulator. Afzal and Sharma [27] designed a MH reactor integrated with hexagonal honeycomb aluminum fins and analyzed its performance under different operating conditions. Results showed that the added fins enhanced the performance of the reactor where during 7200 s, the completed hydrogen absorption reached 90% with an optimum operating pressure of 35 atm and water as the HTF at ambient temperature. Bai et al. [28] introduced a new design for fins having a tree-shaped structure, attached to a central HT tube acting as a stem and containing the HTF (**Figure 3**). Results revealed that for the saturation of hydrogen in the MH bed reaching 90%, the hydrogenation duration for the case of tree-shaped fins compared to the case of radial fins is reduced by 20.7%. The concept of embedding spiral fins was investigated by Chang et al. [29]. The study involved the comparison between different configurations based on the spiral cycle (SC), fin number (FN) and fin thickness (FT). It was shown that as SC increases, the rate of the reaction increases with no effect on the hydrogen storage density; however, the rates of absorption and desorption increased 53.1% and 34.7%, respectively, as the FN increased from 4 to 16, on the expense of a significant reduction in hydrogen storage density reaching 24.1%. Finally, the optimized design and its respective optimal operating conditions were concluded to be: 8 fins with a spiral cycle equals to 1 and a fin thickness of 1 mm, operating at 1 MPa pressure and 273.15 K HT wall temperature for hydrogenation, and 0.1 MPa with 353.15 K wall temperature for dehydrogenation.

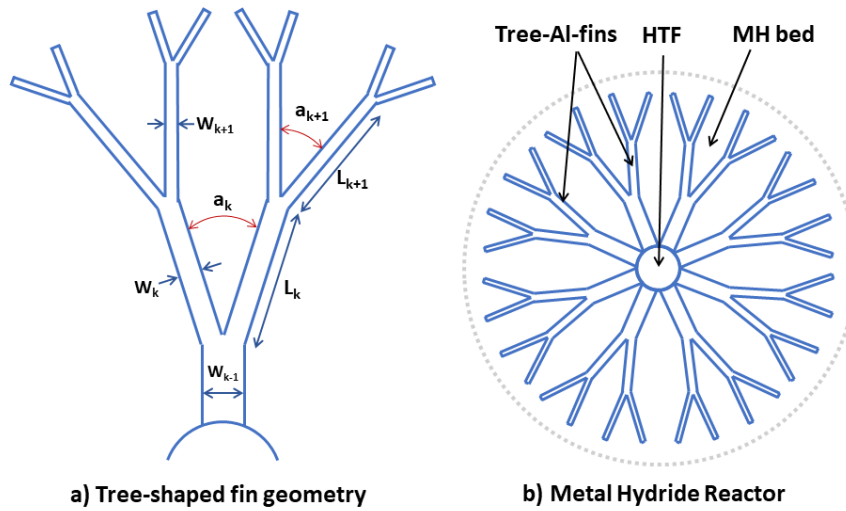


Figure 3 Tree-shape finned MH reactor [28].

2.3 Addition of HT enhancement material to MH bed

As a technique used to overcome the low thermal conductivity metal hydrides have ($\sim 1 \text{ W/m.K.}$), the addition of heat transfer enhancement materials (such as metal foams and expanded graphite...etc.) became a recent method to assess and optimize. Atalmis et al. [30] studied the effect of coating a MH bed with copper which in turns increased the thermal conductivity of the MH bed by a factor of 8. Results showed that the addition of copper coating improves the temperature distribution in the reactor bed, despite the decrease in the hydrogen storage capacity. Kort et al. [31] reviewed recent studies on enhancing thermal conductivity of complex MH by the formation of nanocomposites and the use of nanostructures. Afzal et al. [27] reviewed different HT enhancement techniques for the improvement of the MH adsorption and desorption. It was emphasized that the addition of thermal conductivity enhancing materials (such as copper wires, nickel foam, aluminum foam, graphite flakes and expanded graphite) reduces the MH bed thermal resistance and thus improves hydrogen storage and release. The main drawback that must be taken into consideration during the design is the respective decrease gravimetric and volumetric capacities. Also, the study mentioned that the improvement of the M performance requires simultaneous enhancements in thermal conductivity of the MH bed and heat transfer coefficient related to the HTF, where no remarkable improvement is observed while treating one parameter only. For precise assessment of the dynamic MHHST performance, Bai et al. [32] developed a 3D analysis model to predict the overall equivalent thermal conductivity of the MH bed embedded with HT enhancing materials. The proposed model showed agreement with experimental data, and is recommended for the cases of porosity ranging from 0.33 to 0.68.

2.4 Coupling MH reactor with TES

Thermal energy storage (TES) is used in MHHST to absorb the heat during the exothermic reaction and release it back during its reverse. TES is divided into two categories: Thermal and Chemical with their subcategories shown in **Figure 4**. Thermal energy storage may be Sensible using material with high thermal capacity such as water, rock and soil, or Latent using phase change materials (PCM). The use of sensible energy storage requires the integration of a large storage reservoir coupled to the MH storage tank. Tiwari and Sharma [33] investigated the performance of a MH reactor integrated with a thermocline-based TES system. The study utilized water as the sensible TES material and aimed to assess the effect of charging supply pressure, pressure during stratification and discharging pressure on

the MH performance. Preliminary results revealed a storage efficiency of 81.7% for a supply pressure of 16 atm. Also, it was shown that the discharging efficiency exceeded 70% where the sensible storage TES medium was able to supply the MH bed with 60% of the needed desorption energy.

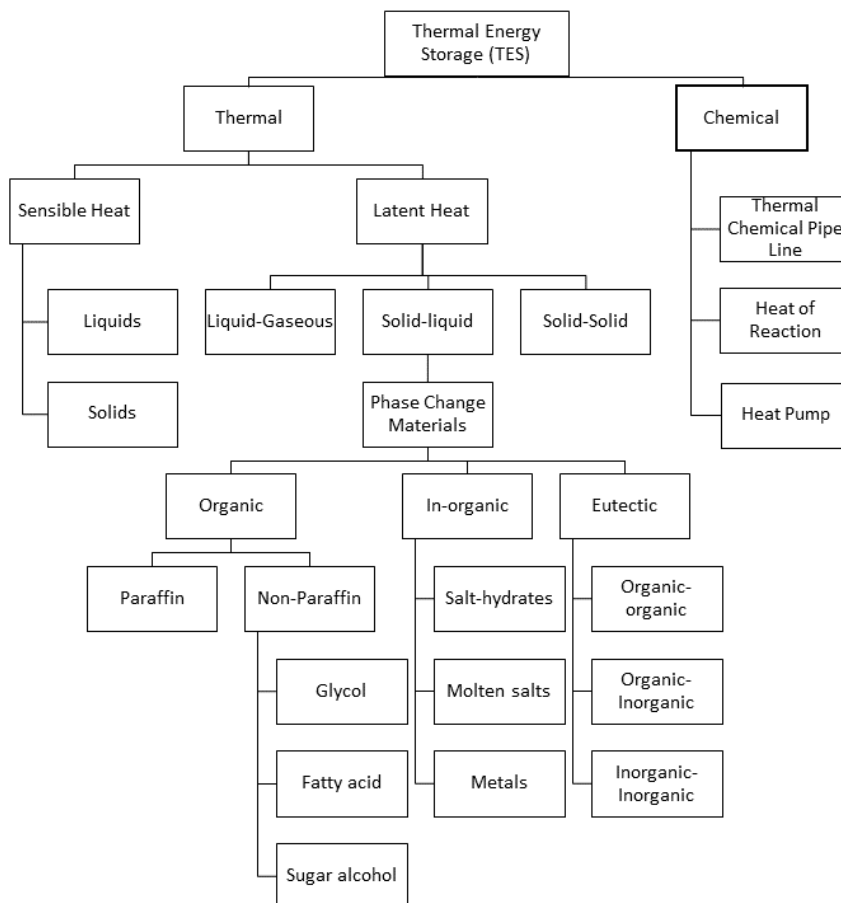


Figure 4 TES and PCM classifications [34].

Utilizing PCMs in MHHST is limited to those having their transition phases as solid-liquid, which are classified into three subcategories: organic, inorganic and eutectic PCMs [35]. Organic PCMs such as paraffins are known for their high latent heat of fusion and wide temperature range. Organic PCMs possess thermal stability as they have no supercooling nor phase separation problems. However, their disadvantages are mainly their low thermal conductivity and leakage possibility while being in liquid phase [36]. On the other hand, inorganic PCMs have relatively high thermal conductivity, a wide range of operating temperatures and high latent heat, but still accounting for the problems of corrosion, short term energy storage (i.e.: phase separation and high supercooling), and liquid phase leakage [37], [38]. The problems addressed regarding organic and inorganic PCMs can be mitigated by combining two different PCMs to form a eutectic PCM. By proper selection of the ingredients of the eutectic PCM, one can target specific applications in terms of operating temperature and required enthalpy. However, the main issue while using eutectics is the poor knowledge of their thermophysical properties [36].

The concept of using TES is directly related to the nature of the MH hydrogen storage reaction (i.e.: being exothermic with an endothermic reverse). It is crucial that upon the exothermic release of heat during hydrogenation in the MH bed, a continuous expulsion of heat must be present so that the reaction remains in progress. At this stage the PCM absorbs the expelled heat and stores it in the form of latent energy while undergoing phase transition to liquid. Then, during dehydrogenation, the PCM solidifies by releasing the stored heat required for the MH bed for desorption reaction [14] Studies addressing the

use of PCMs for thermal performance enhancement of MH reactors are discussed thoroughly in the upcoming sections, forming the core and major contribution of this article. Yet, two studies are mentioned here for the coherence of the current section topic. Yao et al. [39] proposed a novel MH reactor coupled to a salt-hydrate PCM for a fuel cell application. The MH bed was packed in a metallic tank which in turns was surrounded by a PCM layer. The study comprises a 3D model to investigate the effect of operating pressure and thermophysical properties of the PCM (namely: enthalpy, conductivity and melting temperature). Results showed the efficiency of hydrogen adsorption is directly related to the supply pressure where an increase in the pressure is followed by a respective increase in the efficiency. Proper selection of PCM such that the crystallization temperature and thermal conductivity are moderate results in MHHST efficiency enhancement. Finally, the experimental results revealed that the application of the proposed system coupled to PCM in fuel cell triggers a stable hydrogen storage efficiency of about 60% indicating an autothermal-equilibrium performance. Alqahtani et al. [40] altered the conventional design of the PCM-MH reactor by adding PCM in the center of the reactor rather than placing PCM only on the circumference (refer to **Figure 5**). The resulting design comprises a MH bed sandwiched between to layers of PCM thus increasing the HT area. Results showed a reduction in hydrogen adsorption and desorption durations of 81.5% and 73%, respectively, for the proposed configuration compared to the conventional design.

It is of valuable importance to select PCMs for acquiring a higher MHHST performance level. The selection of PCM is related to its thermo-physical, chemical, kinetic, economic and environmental properties. The prior property under consideration is the melting/solidifying temperature. The melting point of the PCM should be less than the hydriding temperature [14]. In addition, referring to the targeted application, the selection of the MH bed material is essential knowing that metal hydrides are classified into two categories: low temperature storage MH and high temperature storage MH.

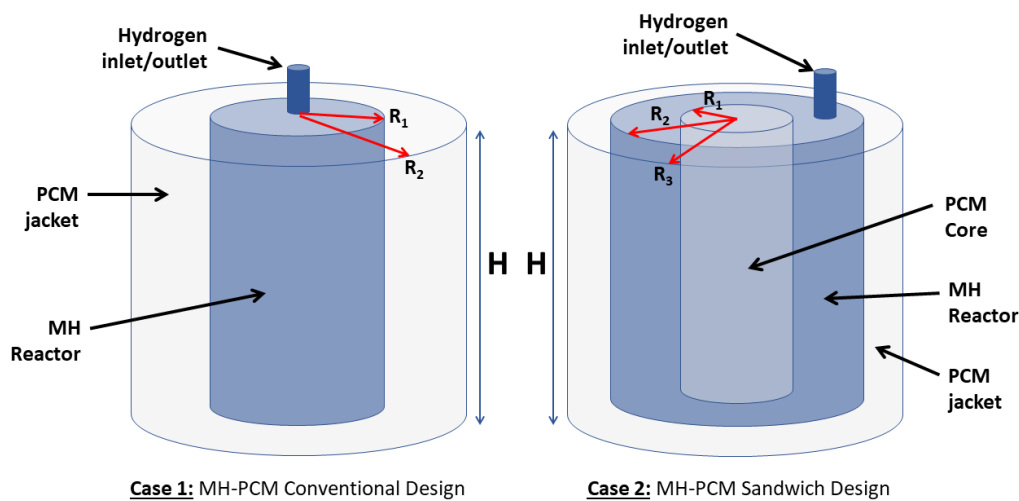


Figure 5 Conventional and proposed MH-PCM systems [40].

The concept of introducing chemical thermal energy storage for enhancing the performance of MH reactor is mainly, but not limited to, coupling with reactive metal compounds such as metal chlorides, knowing that MH is one of the chemical energy storage materials. Shi et al. [41] performed a numerical and analytical study on the performance of a disk MH reactor coupled to MgO TCM storage system. As mentioned by the authors, the advantage thermochemical material (TCM) has over PCM is its higher energy density, leading to smaller reactor size (enhanced compactness). The selection of the MH and the TCM is done on the basis of combination viability related to the equilibrium temperature range. Results showed that the desorption duration is decreased by the increase of the permeability of Hydrogen in the MH bed. Also, it was shown that the thermal performance of the reactor is enhanced in terms of hydrogenation and dehydrogenation durations by the addition of metal foams, however, the hydrogen

production is slightly decreased. Chang et al. [42] enhanced the conventional design of the MH-TCM system by the addition of an internal cylindrical TCM layer, similar to that proposed by Alqahtani et al. [40] in the case of MH-PCM reactor. Results showed that, compared to the conventional design, the MH-TCM sandwich system possesses higher rate of reaction and enhanced heat transfer which is triggered by the larger HT area and relatively higher thermal conductance. As a consequence, a reduction of 61.1% is in the hydrogenation time is obtained.

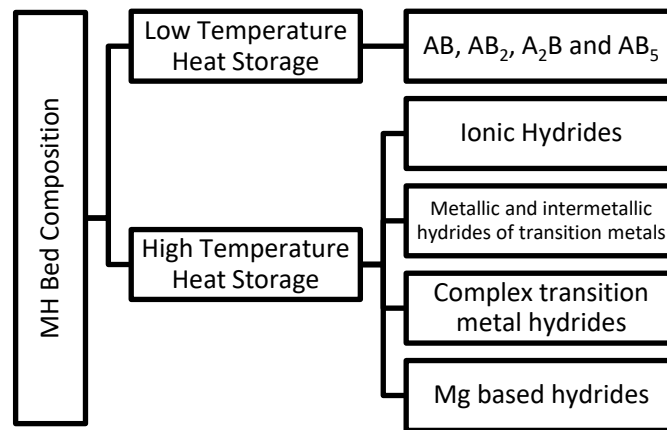


Figure 6 MH bed used materials [43].

The aforementioned methods imply promising thermal management enhancements for MH reactors. Further comparisons between the different methods are presented in **Table 1**. The table infers that there is no best one method to be followed while designing the MH reactor. The hybridization between these methods is the key solution for optimizing the MH performance and alleviating the adsorption and desorption of Hydrogen.

Table 1 Heat Transfer enhancement technique: advantages and limitations.

Heat Transfer enhancement technique/method	Advantages	Effectiveness	Limitations	Ref.
Metal Fins	Thermal bridging	up to 85% in efficiency	- Homogeneous distribution of alloy is affected in case of transverse fins - Reduction in overall volumetric and gravimetric MHHST capacity.	[14], [44]
Expanded graphite and Metallic composites	Thermophysical properties enhancements	increases thermal conductivity over 32 W/m.K.	- Homogeneous distribution of alloy is challenging. - Short-term life cycle due to disintegration from the MH bed.	[14], [44]
Metal foams (MF) with porosity	Thermophysical properties enhancements	increases thermal conductivity over 10 W/m.K.	- effects on adsorption/ desorption rates. - accumulation of alloy in the MF in case of small pore size	[14]
Shell and tube reactor with the tubes hosting the MH	Homogeneous distribution of MH alloy	-	-	[14]
Embedded Tubes of HT fluid in a hosting MH	Reducing pathways between cooling surfaces	-	-	[14]
Coupling the MHHST with PCM	Controlling the temperature and eliminating parasitic energy	-	- Heat transfer resistance due to low thermal conductivity of PCM. - Decrease in hydrogen storage volumetric and gravimetric capacity.	[14], [44], [45]

3. Discussion

The use of metal hydrides in storing hydrogen rely on the proper management of adsorption and desorption and the efficiency of these processes. Convenient thermal management using fins, advanced heat exchanger, incorporating HT enhancers and PCMs leads to upgraded effectiveness in-terms of hydrogenation and dehydrogenation rates, capacity and control. From the aforementioned articles, it is clear that the experimental methodology is lacking with concentration on simulations and numerical computations. Also, the non-technical aspects such as environmental and economic studies need further analysis. Coupling different techniques to form hybrid MHHST is promising and requires attention. On the PCM scale, the integration of multi-PCM layers is of valuable importance as different melting temperature enhances the control of adsorption/desorption. Finally, the integration of MHHST within specific applications such as the fuel cell, give much clear evidence about the success of the introduced thermal management method, and also needs further research.

4. Conclusion

To sum up, hydrogen storage using metal hydrides show promise as a sustainable energy carrier alternative, especially for fuel cell systems. The current article reviewed recent advancements in thermal management of metal hydride reactors. Different thermal management enhancement techniques used in active and passive applications of MHHST are highlighted including: Finns, HT enhancers, Advanced heat exchanger with relevant HTF, and integration of PCM-TES. Recent experimental and theoretical studies on the use of PCM in chemical MH hydrogen storage are compared. The promising feasibility of combining all four thermal management techniques indicate the need of further numerical, simulation and experimental studies for optimizing thermally managed-MHHST.

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